Investigation of pH and mCO_2 influence on Gd^{3+} and UO_2^{2+} sorption onto goethite and nontronite

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REE and U are important constituents of radioactive wastes. Goethite and the clay mineral, nontronite, could form during corrosion of waste-package components buried in underground radioactive waste repositories. Adsorption onto secondary reaction products may result in the retention of U(VI) and Gd in or near the waste-package. CO_2 is a common component in underground aquifers. It interacts with REE and UO_2^{2+} forming carbonate species and absorbs onto mineral surfaces changing their adsorption properties. Investigation of REE and UO_2^{2+} behavior in carbonate iron-bearing suspensions is of interest to models of risk assessment of permanent storage of radioactive wastes in geologic formations.

Experiments were carried out at discrete concentrations of CO_2 (0.001-0.03 mole/kg H_2O) in 0.1*m*NaCl solution. CO_2 was loaded into the suspension as a Ar-CO_2 gaseous mixture. The partial pressure of CO_2 was determined through the potentiometric measurement of a control solution equilibrated with the gaseous phase during the set of experiment. It is found that adsorption of Gd^{3+} and U(VI) onto goethite and nontronite increases in the range of pH from 4 to 6 with an increase of mCO_2. In case of U(VI), adsorption decreases with increasing mCO_2 at pH>6. Adsorption of U(VI) onto goethite increases again at pH>10 and mCO_2=0.03. Various surface complexation modeling approaches were used to describe the Gd^{3+} and U(VI) experimental data.

Adsorption of Lanthanum to goethite in the presence of gluconic acid

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Trivalent lanthanide and actinide elements in radioactive waste can pose risks to humans and ecological systems for many years. Organic complexing agents can alter the mobility of these elements. The poly-hydroxycarboxylic acid, gluconic acid, has been used as a structural analogue for cellulose degradation products, common in waste-disposal facilities. We studied the effect of the gluconate anion on the adsorption of lanthanum to goethite. Batch pH adsorption edge experiments were conducted with lanthanum in the absence of gluconate, and with lanthanum and gluconate at a 1:1 mole ratio. Lanthanum concentrations studied were 0.1, 1, and 10 mM, covering a range from 10% to 1000% of the calculated available adsorption sites on goethite.

In the absence of gluconate, lanthanum was primarily present in solution as free lanthanum ion. In the presence of gluconate, free lanthanum concentration in solution decreased with increasing pH as step-wise deprotonation of the gluconate molecule increased the fraction of lanthanum complexed with gluconate. Adsorption to the goethite surface was represented with the diffuse double-layer model. The number of adsorption sites and the intrinsic binding constants for the surface complexes were estimated from the pH adsorption edge data using the computer code FITEQL 4.0. Two surface reactions were used to fit the adsorption data in the absence of gluconate. A strong binding site with no proton release and a much higher concentration of weak binding sites with release of two protons per lanthanum adsorbed.

The adsorption of lanthanum was not measurably affected by the presence of gluconate below pH 7. At pH values above 7, however, gluconate doubled the maximum amount of lanthanum adsorbed. The presence of gluconate did not appear to inhibit the formation of solid lanthanum hydroxide at elevated pH and millimolar lanthanum concentrations. The effect of organic molecules on the mobility of trivalent lanthanides and actinides cannot be simply described with equilibrium thermodynamic models based on currently available data.